Comparison and Development of Absorption Peak Determination Algorithms for Wavelength Standards

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ABSTRACT

Several peak determination algorithms are described and compared using the spectra of a NIST wavelength / wavenumber standard reference material (SRM). These methods are the (1) centroid (or center of gravity) (with fraction value 0.5), (2) extrapolated centroid, (3) extrapolated bisecting, (4) polynomial curve fit, and (5) absolute maximum (minimum) methods. Comparisons are made of the peak wavelength value accuracy and reproducibility, versatility and other aspects of the peak determination methods. Optimization studies of the centroid, extrapolated centroid and extrapolated bisecting peak determination methods, used for several NIST SRM's, have found that the peak value accuracy and precision can be improved by careful selection of peak fraction, spectral data density and polynomial fitting order (for extrapolated algorithms).
Key words: peak determination method, wavelength or wavenumber standard, centroid or center of gravity, extrapolated centroid, peak maxima or minima, extrapolated bisecting, IR, NIR, FT-IR, polynomial curve fit

1. INTRODUCTION

The centroid or center of gravity method[1] is a peak (absorption line) evaluation algorithm that has excellent reproducibility (less sensitivity to noise).[2] Its use has become more widespread since NIST began providing the polystyrene Standard Reference Material (SRM) 1921a (with fraction value $f = 0.5$) for calibrating the wavenumber or wavelength scales of spectrometers in the mid-infrared region,[3] and for the certified values of rare-earth-oxide-doped glass SRM 2035 for the near-infrared region[4] (with $f = 0.1$). The good reproducibility of the peak values from the centroid method is a consequence of the large number of data points used in its calculation and the accompanying averaging out of the noise. The greater the number of spectral data points used in the peak evaluation process the less the effect of noise on the peak value. Similarly, the larger the peak fraction, f, used in the centroid method, the less the centroid value obtained is affected by noise in the spectrum. In addition, an appropriate level of zero-filling or interpolation of a Fourier transform or dispersive spectrum can reduce error due to its discrete nature.[5]

As demonstrated in its use with SRM 2035,[3] and also in Section 4 of this paper, the reproducibility of the centroid method is about 4 to 10 times better (in standard deviation of a number of measurements) than that of the most popularly used absolute peak maximum (minimum) evaluation method. However, the centroid method has other important features that need to be considered when comparing to other methods. Foremost of these is that, by definition, the line centroid value and line minimum values are different physical quantities, and only equal for perfectly symmetrically shaped lines. Hence, a direct comparison of values for centroid and other methods is not necessarily meaningful. Thus, for users of NIST wavelength SRMs that only have access to other wavelength evaluation methods, the certified centroid values are of limited benefit. This situation is slowly being remedied through the proliferation of the centroid method.[6] Another significant difference between the centroid and other methods is its sensitivity to photometric scale (y-axis) error. Each data point of a peak (line) within the spectral range defined by the peak fraction contributes to the peak centroid value. Thus, a relative error in the y values (due to detector non-linearity, detector nonequivalence, inter-reflections, interference fringe effect, etc.) will result in an error of centroid value of the line. In addition, the spectral backgrounds adjacent to the line determine the line depth (peak height) and hence the line (peak) fraction associated with each data point of the line. So relative errors in the backgrounds can also result in error in the centroid value.

Optical Diagnostic Methods for Inorganic Materials II, Leonard M. Hanssen, Editor,
Proceedings of SPIE Vol. 4103 (2000) © 2000 SPIE. · 0277-786X/00/$15.00

To overcome these problems of the centroid method and also to accommodate users who only have access to software designed to locate line minima (peak maxima), we have developed an extrapolated centroid (EC) method and an extrapolated bisecting (EB) method. These two new peak picking algorithms combine the advantages of the centroid method with a line minimum (peak maximum) locating capability.

As implied by its name, the EC method determines a peak value through an extrapolation procedure. The peak maximum (minimum) is determined by curve fitting a series of centroid values obtained with different peak fractions, f and extrapolating to $f = 0$. To reduce the error in the extrapolation due to the increased effect of noise in the spectrum at smaller peak fractions, a chi square (X^2) fit is employed. The curve fit uses weighting by the inverse of the standard error of a set of 6 measurements of the same sample.

The EB method we use is a refinement of the 'bisecting method' used for NIST wavelength SRM's 2034[7] (ultraviolet) and 1920[8] (near infrared reflection). The bisecting method is a graphical method obtained from the older spectrometer output format of a recorded chart. A series of pencil lines are drawn parallel to the x-axis across a peak. Points half way across the peak are marked on these lines. Finally, a line is drawn through these points, resulting in an intersection with the spectral curve. The x-axis value of the intersection is the peak value given by the method. The EB method is an enhanced programmed version of the bisecting method. The EB method uses extrapolation of a curve fit through the series of bisecting points to determine the peak maximum (minimum). The bisecting points are determined for an equally spaced series of peak fraction values, f. To reduce the effects of noise, curve fitting is used to determine all intersections in the method, including the points along the spectrum used for determining the bisecting values as well as the intersection of the extrapolated curve with spectrum to give the peak value.

Detailed descriptions of the EC and EB methods can be found in other publications.[9,10] In this paper we present results of a parameter and intercomparison study using a data set of infrared polystyrene spectra obtained for the calibration of NIST SRM 1921a. In Section 2 measurement conditions and analysis routines are described. An analysis of critical process parameters and their effects on peak values of EC method is presented in Section 3. And a comparison of peak values obtained from the centroid, EC, EB, polynomial curve fit, and absolute line minimum (peak maximum) methods are presented in Section 4.

2. EXPERIMENTAL AND DATA PROCESSING CONDITIONS

All results are based on the interferograms obtained from twelve polystyrene samples that were measured in sequence six times (72 measurements in all) under vacuum using a Bomem DA3 FT-IR spectrometer.[3] The instrumental conditions used in the raw interferogram acquisition were: resolution, $r = 0.5$ cm^{-1}, sample spot size diameter = 1 mm, scan speed = 0.5 cm/s, gain = 4, number of scan = 100, KBr beamsplitter, globar source, and MCT detector.

In order to eliminate the effects caused by measurement-to-measurement variations, a single set of 72 interferograms was used to derive four sets of 72 spectra: two sets at $r = 0.5$ cm^{-1} with Boxcar truncation and Hamming apodization, and two sets at $r = 4.0$ cm^{-1} with Boxcar truncation and Hamming apodization. Zero filling was used to maintain a constant data interval (x-axis) for all spectra independent of resolution (see Section 3). For the centroid method evaluation (with $f = 0.5$), the data spacing for spectra taken at a nominal resolution of 0.5 cm^{-1} with the typical zero fill factor of 2, is 0.241 cm^{-1}. Since the other methods use fewer data points (such as in the extrapolated methods with small peak fraction), for the intercomparison study, the original interferograms are zero filled 16 times resulting in spectra with a data interval of 0.013 cm^{-1}.

For the intercomparison and parameter studies, the EC and EB values of each of the 13 calibrated line positions are obtained from each polystyrene transmission spectrum. They are evaluated using line fractions, f, ranging from 0.5 down to 0.05 in 0.05 steps. The curves of wavenumber value, ν vs. f of the 13 polystyrene lines can be approximated by polynomials up to third order (for the fraction range 0.05 to 0.5): first order for lines nominally located at 842 and 2849 cm^{-1}; second order for those at 906, 1154, 1583, 1601, 3001, 3026, 3060 and 3082 cm^{-1}; and third order for those at 545, 1028 and 1069 cm^{-1}.

3. EFFECTS OF APODIZATION, RESOLUTION, FRACTION RANGE AND DATA DENSITY USING THE EC METHOD

The effects of apodization, resolution and fraction range on peak values obtained by the EC method are shown for the 1583 cm^{-1} band of polystyrene in Figure 1. Results from all 72 measurements are shown. The following can be observed about the spread of the EC peak values. (1) Higher resolution data ($r = 0.5$ cm^{-1}) exhibit more spread than lower resolution data ($r = 4.0$ cm^{-1}) for both Boxcar and Hamming apodization for constant fraction range. (2) Hamming apodization data has slightly less spread than Boxcar data for constant resolution and fraction range (refer to the calculated standard deviations shown in legend for more detailed comparisons). (3) The mean values for both fraction ranges are essentially the same. Hence the extrapolation method works well relatively independent of the fraction range used. (4) The larger fraction range data for $r = 0.5$ cm^{-1} exhibits considerably less spread than the smaller range data. Spectral noise information is mainly distributed in the tails of an interferogram. Apodization was primarily designed to suppress side-lobes resulting from the FT of a truncated interferogram. At the same time, an apodization function can suppress noise as well as degrade the effective resolution of the original interferogram. The larger fraction range used for curve fitting has more data points at higher peak fractions, for which the reproducibility is better. Hence the data spread should be less for the larger range data, as seen in Fig. 1. A 0.1 cm^{-1} difference is observed between the EC values for $r = 4$ cm^{-1} with Hamming apodization and other three combinations in both Figure 1a and b. Similar or larger shifts are found for a number of lines in the polystyrene spectrum. This is due to the reduction of the effective resolution that results in significant distortion of the line for $r = 4$ cm^{-1} with Hamming apodization. Therefore this combination has been dropped from further study.

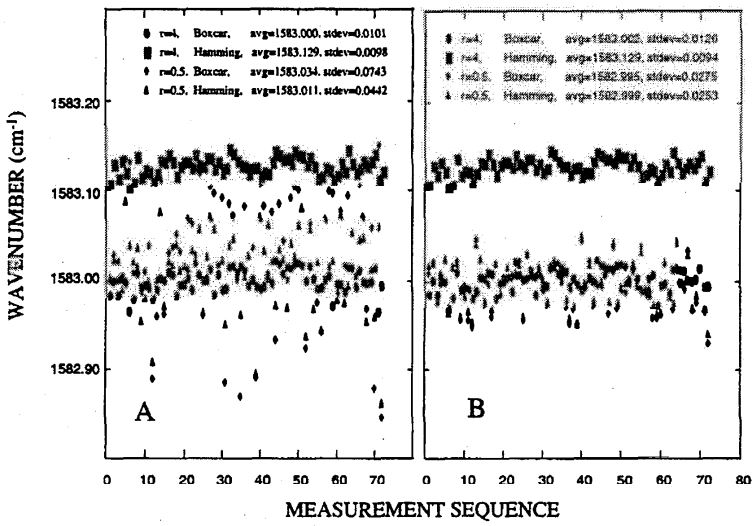

FIGURE 1. Comparison of EC method values for the four combinations of $r = 0.5$ cm^{-1} and 4 cm^{-1}, and Boxcar and Hamming apodizations, for the 1583 cm^{-1} line of polystyrene for fraction ranges of (A) 0.01 to 0.10 and (B) 0.05 to 0.50. The results of all 72 measurement are shown. In the legend, "avg" stands for the mean of 72 measurements and "stdev" stands for the corresponding standard deviation.

The EC method, as has been demonstrated for the centroid method,[9] is sensitive to the spectral data interval and the actual data point locations on the x-axis. The maximum variations of the EC peak values due to shifting of the data points along the x-axis is shown in Figure 2 for all 13 polystyrene peaks. These

are obtained and plotted for a number of spectral data spacing intervals. It is clear from this plot that the maximum EC peak shifts of all polystyrene bands decrease when the spectral data spacing decreases.

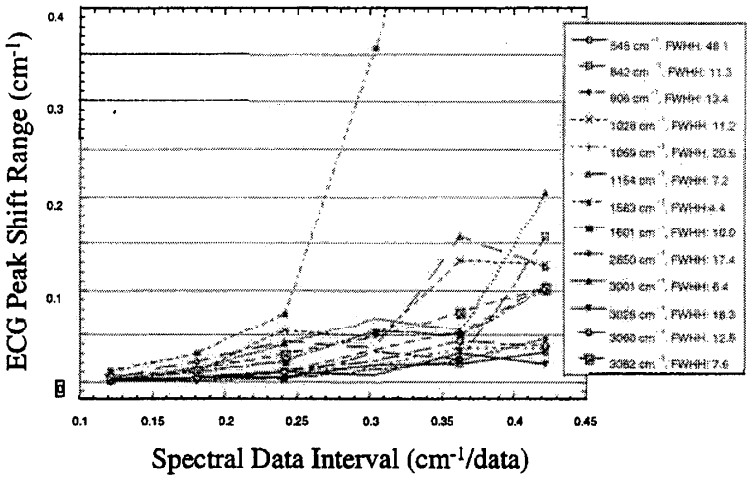

FIGURE 2. Maximum peak value error (using the EC method) due to data point location along the x-axis for 13 peaks of polystyrene as a function of spectral data spacing. FWHH stands for full width at half height of the peak.

Thus, by sufficiently reducing the data interval, the error due to discrete nature of spectrum can be effectively eliminated. One can also note from Fig. 2 that the narrower the line, the greater the error due to a finite data interval. In Section 4, spectra with data interval of 0.013 cm^{-1} are used to guarantee an insignificant error contribution.

4. COMPARISON OF PEAK VALUE DETERMINATION METHODS

We compare seven peak (absorption line) evaluation methods in this study. They are briefly described as follows. (1) The EC method with 2nd and 3rd order weighted polynomial fit using a fraction range of 0.05 to 0.5 in steps of 0.05. (2) The EB method with 2nd order polynomial fit and the same fraction level as used in the EC method. (3) A thirty point quadratic fit to the bottom of the line. (4) A four point cubic spline fit (essentially an absolute peak minimum value method). (5) The Grams[11] (version 4) peak evaluation method with 49 data points used in smoothing. (6) The Grams (version 4) peak evaluation method with no smoothing (the absolute peak minimum value method). (7) The centroid method with fraction 0.5 (for reference , but not direct comparison). Comparisons are made using three sets of 72 spectra with the following conditions: (A) $r = 0.5$ cm^{-1} and Boxcar truncation, (B) $r = 0.5$ cm^{-1} and Hamming apodization, and (C) $r = 4.0$ cm^{-1} and Boxcar truncation.

Comparisons for three absorption lines of the polystyrene spectra 1601 cm^{-1}, 2850 cm^{-1}, and 3001 cm^{-1}, are shown in Figures 3, 4 and 5, respectively. The following observations can be made about all three figures: (1) The average values of the EC and EB method values are within 0.02 cm^{-1} of the absolute line minimum value methods. (2) The standard deviations of peak values of the 30 point quadratic fit, 4 point cubic spline fit and Grams 0 point smoothing methods, decrease dramatically going from A to B to C. (3) The centroid values are significantly different from the other 6 method results. (4) The EC and EB method

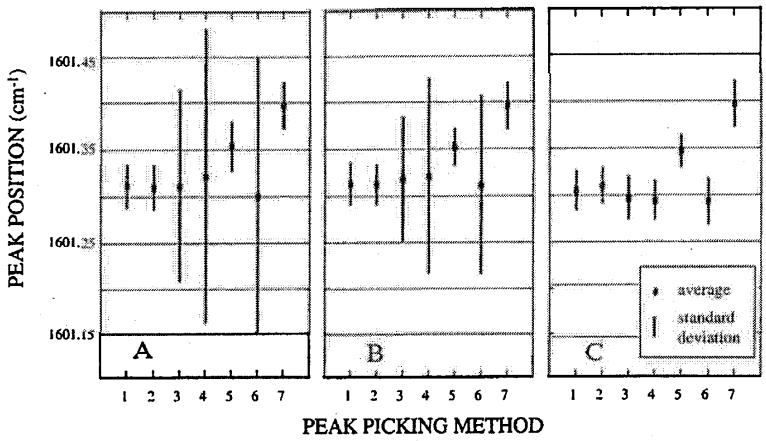

FIGURE 3. Comparison of line positions determined by different peak evaluation methods for the 1601 cm^{-1} line of polystyrene where: (A) r = 0.5 cm^{-1} and Boxcar truncation, (B) r = 0.5 cm^{-1} and Hamming apodization and (C) r = 4.0 cm^{-1} and Boxcar truncation. Peak evaluation methods are listed as 1: EC; 2: EB; 3: 30 point quadratic fit on peak bottom; 4: 4 point cubic spline; 5: Grams 49 point smoothing; 6: Grams 0 point smoothing; 7: centroid. Average and standard deviation were obtained from 72 measurements.

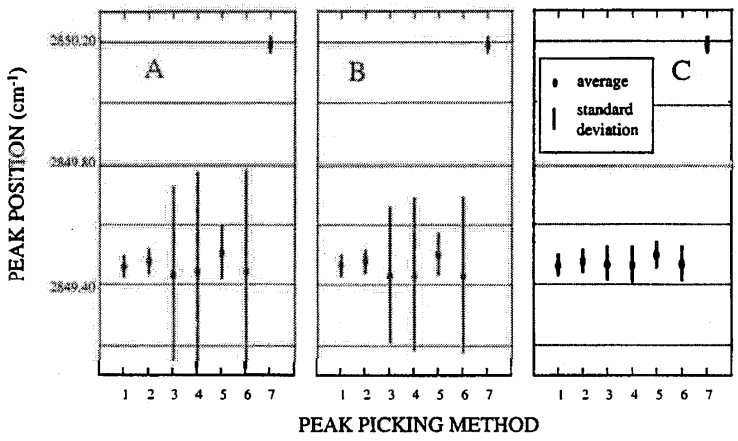

FIGURE 4. Comparison of line positions determined by different peak evaluation methods 3 for the 2849 cm^{-1} band of polystyrene (see Figure 3 caption method) means are with the other methods designed for determining the line minimum value

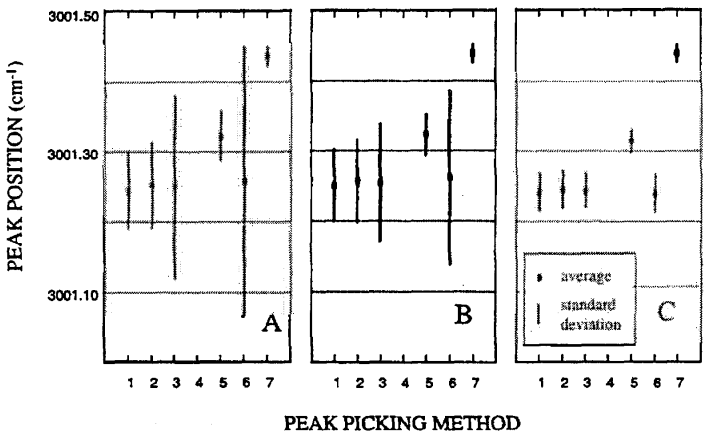

FIGURE 5. Comparison of line positions determined by different peak evaluation methods 3 for the 3001 cm^{-1} band of polystyrene. Note, 4 point cubic spline data was not available for this band.

values are very consistent under all three resolution and apodization combinations. (5) Their (EC and EB method) standard deviations are the smallest of all methods.

5. CONCLUSIONS

Centroid (center of gravity), extrapolated centroid and extrapolated bisecting methods are noise-discriminative and peak shape independent peak evaluation algorithms. With careful selection of peak fraction, spectral data spacing and polynomial fitting order, highly reproducible peak values can be obtained. With the availability of extrapolated centroid and extrapolated bisecting methods, NIST is able to certify wavelength values 'with low uncertainty, which can be compared directly by customers using generally available peak evaluation software. New certified wavelength values can now be added to existing Standard Reference Materials (SRM's) in order to better match user instrumentation (resolution) and software (peak methods). We encourage customers and instrument manufacturers to employ or adapt these three versatile peak determination algorithms.

6. REFERENCES

[1] Although the term 'center of gravity' is often used to describe this method, in this paper we will refer to it as the 'centroid' method. We prefer to use the more technically accurate term 'centroid' because most spectra have no relation to mass, force, or gravity as implied by the term 'center of gravity.'

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